CHEMICAL KINETICS REVIEW

There have been several concepts presented in our study of chemical kinetics. It is all too easy to miss how these concepts are related. Often concepts are compartmentalized and the interrelationships are missed. In other words: the solo multibranched members tend to produce a condition of myopia with regard to viewing the veritable plethora of coniferous and deciduous growth.

With the above in mind we will consider the following reaction,

$$(CH_2)_2O\ (g) \longrightarrow CH_4\ (g) + CO\ (g)$$

with regard to the interrelationships of the following:

1. The instantaneous rate of the reaction at a given time, t.
2. The rate equation for the reaction.
3. The order of the reaction.
4. The half life of the reaction.

1. THE INSTANTANEOUS RATE OF A REACTION.

The instantaneous rate of a reaction at a given time, t, is determined by plotting either the concentration or pressure of a reactant or product vs. time and drawing a tangent line at the point on the resulting curve at time t (Graph 0). The slope of this tangent line will give the instantaneous rate of the reaction, at time t, with respect to (wrt) the reactant or product being graphed. The kinetic data for the reaction is presented in Table I. We will calculate the instantaneous rate at t = 80.0 min.

Table I

Time, min	P[$(CH_2)_2O$], mmHg	P[CH_4], mmHg
0.0	124.94	0.0
10.0	110.74	14.20
20.0	98.21	23.73
40.0	77.23	47.71
60.0	60.73	64.21
100.0	37.54	87.40
200.0	11.22	113.72

NOTE: all graphs start on page 6.

The instantaneous rate with respect to $(CH_2)_2O$ is calculated from the tangent drawn to the $(CH_2)_2O$ curve at 80 minutes. Using the points at the extreme ends of line: (0, 90) and (152, 0).

$$\text{rate} = \frac{-\Delta P_{(CH_2)_2O}}{\Delta t} = \frac{-(90-0)\,\text{mmHg}}{(0-152)\,\text{min}} = \frac{0.59_{21}\ \text{mmHg}}{\text{min}}$$

rate = 0.59_{21} mmHg min^{-1} at t = 80 min wrt $(CH_2)_2O$.

The instantaneous rate with respect to CH_4 can be calculated from tangent line drawn to the CH_4 curve at 80 minutes. Using the points at the extreme ends of line calculate the rate wrt CH_4.

[Answer: based on these two points: (0, 33) and (175, 140). rate = 0.61_{14} mmHg/min at t = 80 min wrt CH_4.]

Note that the two rates are very close and differ by only 3.3 %. How close these two rates are to each other is a function of how the tangent lines are drawn. Ideally, the rates should be the same if the tangents are drawn correctly. One word of caution is needed. The two rates are the same (or very nearly so) because for each mole of $(CH_2)_2O$ that decomposes, one mole of CH_4 is formed. This would not be true for reactions where the mole amounts are different.

2. THE RATE EQUATION

The rate equation, $\text{rate} = kP^m_{(CH_2)_2O}$, is readily calculated from initial rate data. Here the initial pressure of $(CH_2)_2O$ is measured from a tangent line drawn at t = 0. The initial rate is equal to the slope of this tangent line. The graphs for this series of experiments will not be shown. The data is presented in Table II.

Table II

Experiment	$P[(CH_2)_2O]_i$, mmHg	$Rate_i$, mmHg min^{-1}
1	124.94	1.65
2	300.00	3.89
3	500.00	6.58

The exponent m is calculated as follows:

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k\,P^m_{[(CH_2)_2O]_1}}{k\,P^m_{[(CH_2)_2O]_2}};\ \frac{1.65\text{ mmHg min}^{-1}}{3.89\text{ mmHg min}^{-1}} = \frac{k(124.94\text{ mmHg})^m}{k(300.00\text{ mmHg})^m}$$

$$0.424_{16} = (0.416_{47})^m;\ \ln(0.424_{16}) = m\ln(0.416_{47})$$

$$-0.857_{63} = m(-0.875_{95});\ m = 0.979 = 1$$

Using Experiments 2 and 3 verify that m =1.

Since m = 1, then: $\text{rate} = kP^1_{(CH_2)_2O}$

We will use this equation to find k:

$$\text{rate} = kP^m_{(CH_2)_2O};\ \text{from Experiment 1}: 1.65\text{ mmHg min}^{-1} = k(124.94\text{ mmHg})$$

$$k = \frac{1.65\text{ mmHg min}^{-1}}{124.94\text{ mmHg}} = 0.0132\text{ min}^{-1}\ \text{(note the unit for k)}$$

Use the data from Experiments 2 and 3 to find k.

(from Experiment 2, k = 0.0130 min^{-1}
from experiment 3, k = 0.0132 min^{-1})

$k_{average}$ = 0.0131_3 min^{-1}.

deviation, Δ: $0.0131_3\text{ min}^{-1} - 0.0132\text{min}^{-1} = -0.0001\text{min}^{-1};\ \Delta^2 = 4._9 \times 10^{-9}\text{ min}^{-2}$
$0.0131_3\text{ min}^{-1} - 0.0130\text{min}^{-1} = -0.0001_3\text{ min}^{-1};\ \Delta^2 = 1._{69} \times 10^{-8}\text{ min}^{-2}$
$0.0131_3\text{ min}^{-1} - 0.0132\text{min}^{-1} = -0.0001\text{min}^{-1};\ \Delta^2 = 4._9 \times 10^{-9}\text{ min}^{-2}$

$$\Sigma\Delta^2 = 4._9 \times 10^{-9}\text{ min}^{-2} + 1._{69} \times 10^{-8}\text{ min}^{-2} + 4._9 \times 10^{-9}\text{ min}^{-2}$$

$$= 2._{67} \times 10^{-8}\text{ min}^{-2}$$

$$s = \sqrt{\frac{\Sigma\Delta^2}{N-1}} = \sqrt{\frac{2._{67} \times 10^{-8}\text{ min}^{-2}}{3-1}} = 0.0001_2\text{ min}^{-1}$$

The standard deviation, s, is small indicating that k is constant.

3. REACTION ORDER

From the rate equation it is apparent that the reaction is first order with respect to $(CH_2)_2O$ and first order overall. The order of the reaction could also be determined by graphing the original experimental data presented in Table I. We need to add two new columns to the original data set:

$$\ln\left(P_{[(CH_2)_2O]}\right) \text{ and } \frac{1}{P_{[(CH_2)_2O]}}$$

Table III

time, min	$P[(CH_2)_2O]$, mmHg	$\ln\{P[(CH_2)_2O]\}$	$1/P[(CH_2)_2O]$, $mmHg^{-1}$
0	124.94	4.82783	8.0038
10	110.74	4.70718	9.0302
20	98.21	4.5871	10.18
40.0	77.23	4.3468	12.95
60.0	60.73	4.1064	16.47
100.0	37.54	3.6254	26.64
200.0	11.22	2.4177	89.13

By graphing each function of pressure versus time the order of the reaction can be determined. A plot of P vs. time was made in Graph I. Since it did not yield a straight line, the reaction is not zero order. The only plot that will yield a straight line is that of ln(P) vs. time, (Graph II), thus indicating a first order reaction, as expected. The plot of 1/P vs. time does not yield a straight line (Graph III). Thus the reaction is not a second order reaction.

Since the reaction is first order the equation for this reaction can be written as:

$$\ln\left(P_{[(CH_2)_2O]}\right)_t = -k \bullet t + \ln\left(P_{[(CH_2)_2O]}\right)_t$$

From the initial rate data in Table II we determined the average value of the rate constant, k, to be 0.0131_3 min^{-1}. Determine the slope of the line for Graph II. From the slope determine k. Does this value agree with the value calculated from the initial rate data?

[The points I chose were, (0, 4.85) and (200, 2.20) this gives a slope of -0.0132_5 min^{-1} and $k = 0.0132_5$ min^{-1} which agrees quite well with our initial rate calculation.]

Using the point (200, 2.20) we can solve for the intercept: b = 4.85. Our equation is now: $\ln\left(P_{[(CH_2)_2O]}\right)_t = -0.0132_5 \text{ min}^{-1} \bullet t + 4.85$.

4. HALF LIFE OF A REACTION

For a first order reaction, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0132_5\ \text{min}^{-1}} = 52.3\ \text{min}$

Another method for the determination of half life is as follows. The half life of this reaction occurs when the pressure of $(CH_2)_2O$ is equal to one half of the initial pressure. This occurs when P = 1/2(starting pressure). From Table I our starting pressure was 124.94 mmHg. On half of 124.94 mmHg = 62.47 mmHg. We can use our first order rate law to solve for t.

$$\ln\left(P_{[(CH_2)_2O]}\right)_t = -k \bullet t + \ln\left(P_{[(CH_2)_2O]}\right)_t$$
$$\ln(62.47) = -0.0132_5\ \text{min}^{-1} \bullet t + \ln(124.94)$$
$$4.135 = -0.0132_5\ \text{min}^{-1} \bullet t + 4.828$$
$$-0.693 = -0.0132_5\ \text{min}^{-1} \bullet t$$
$$t = 52.3\ \text{min}$$

5. SUMMARY

As we have seen all of the following expressions can be used to describe the reaction:

$$(CH_2)_2O\ (g) \longrightarrow CH_4\ (g) + CO\ (g)$$

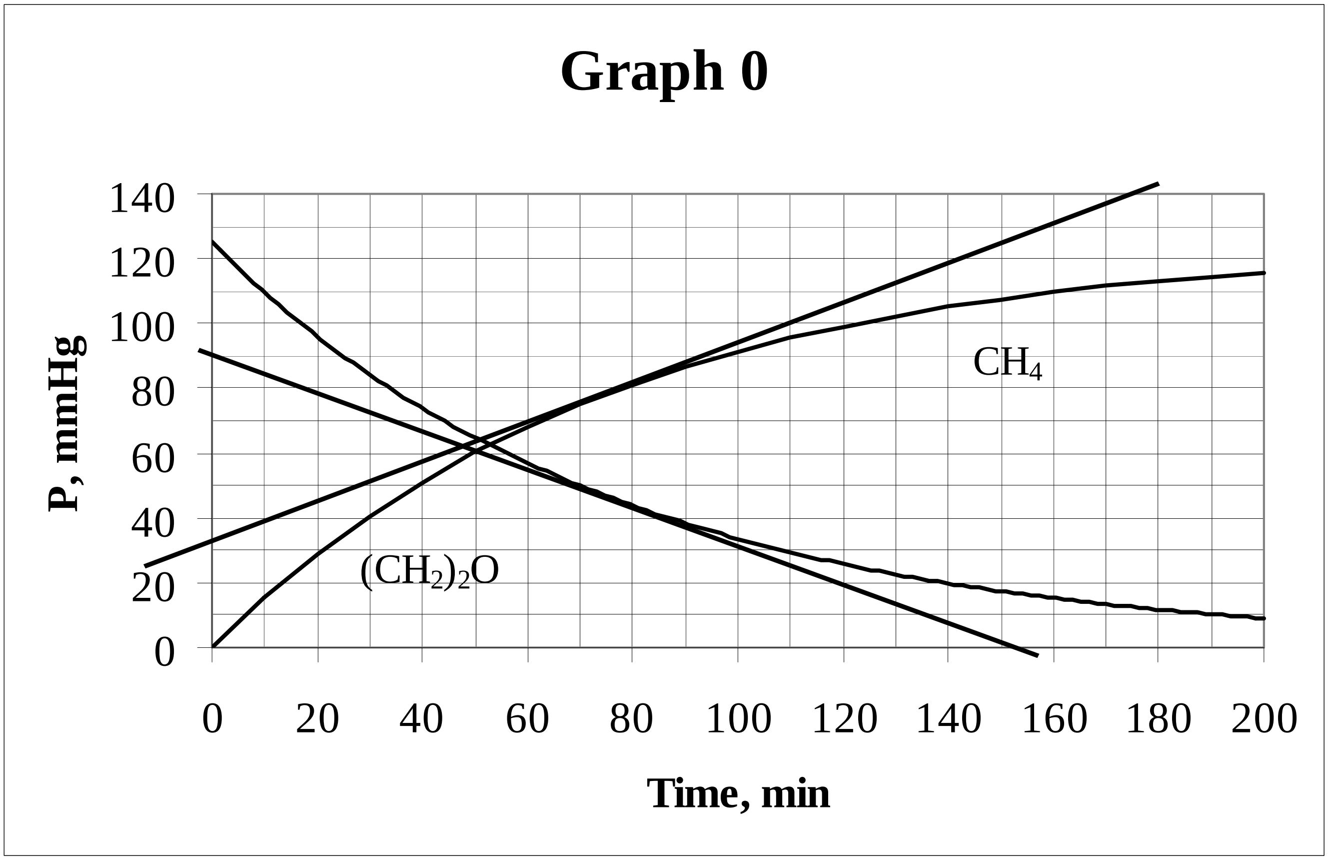
$$\text{rate} = \frac{-\Delta P_{(CH_2)_2O}}{\Delta t};\ \text{rate} = \frac{\Delta P_{CH_4}}{\Delta t}$$

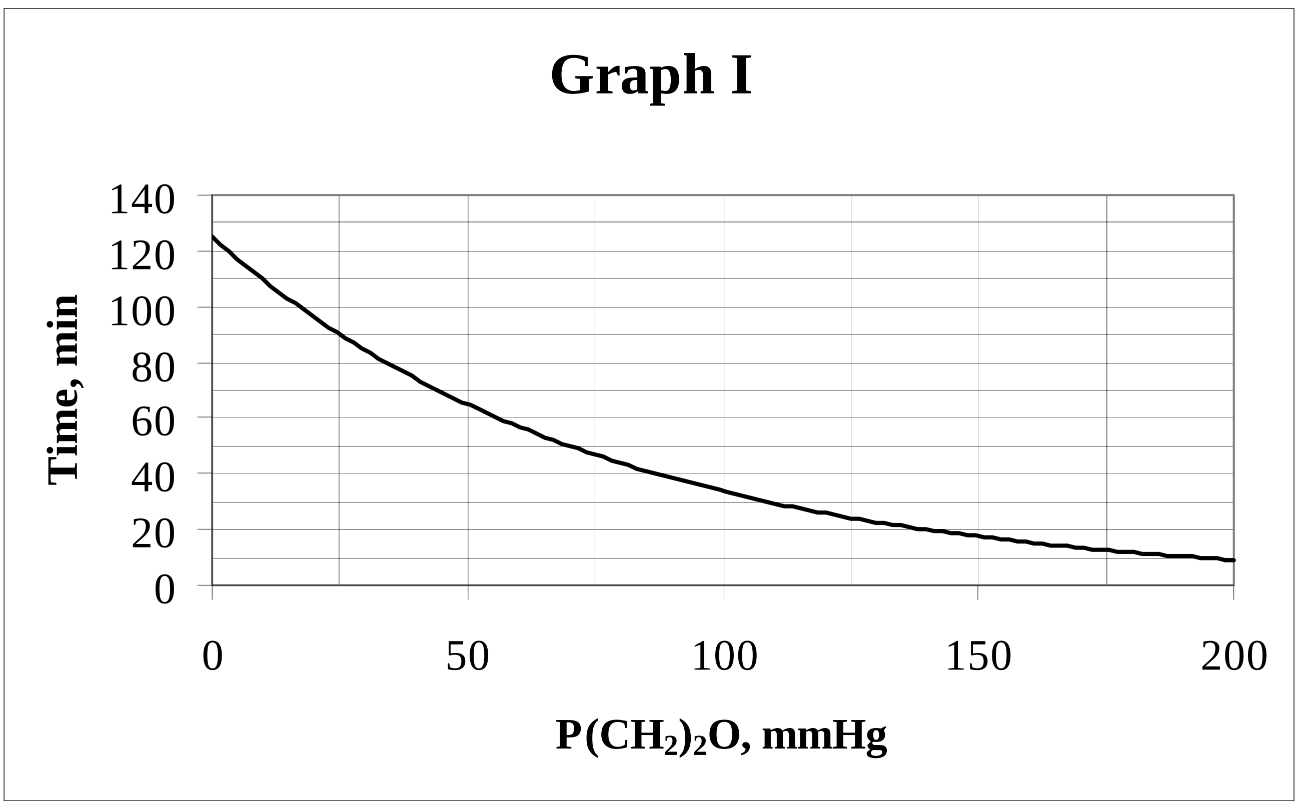
$$\text{rate} = \frac{-\Delta P_{(CH_2)_2O}}{\Delta t} = 0.0131_3\ \text{min}^{-1}\ P^1_{(CH_2)_2O}$$

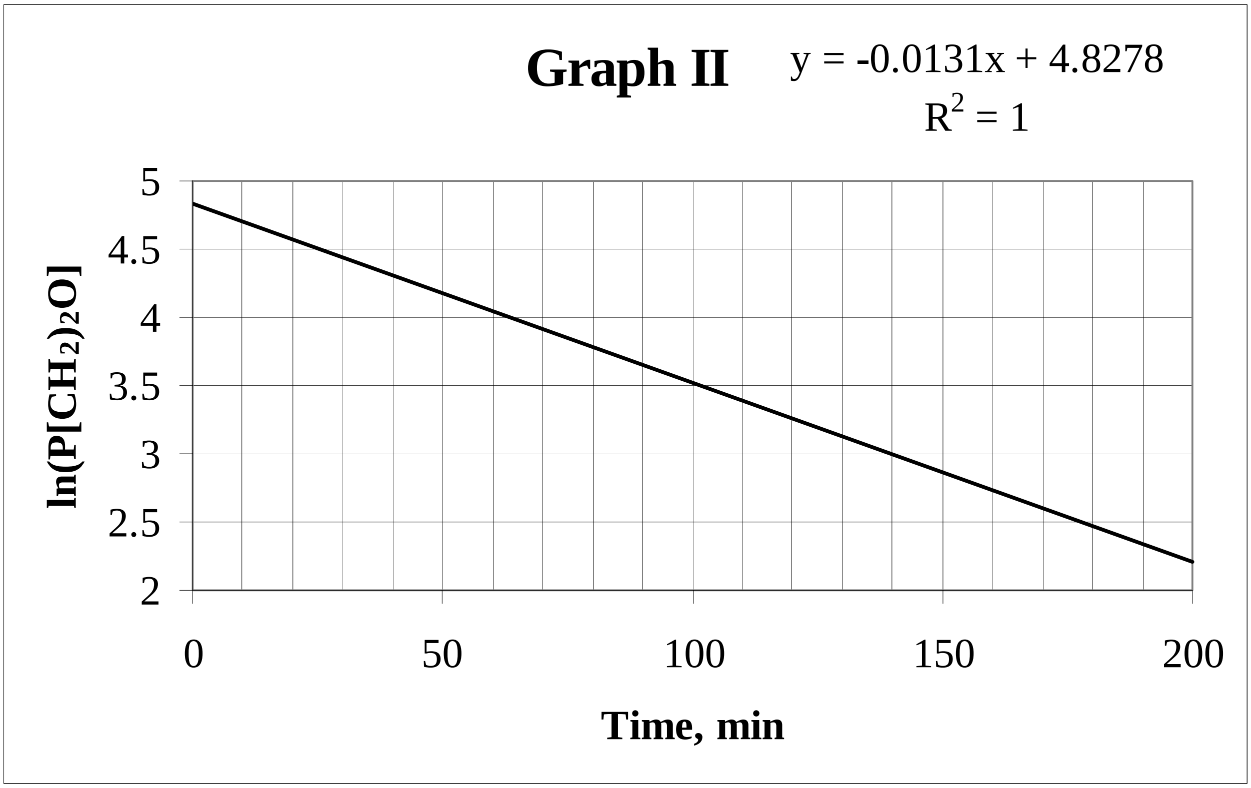
$$\ln\left(P_{[(CH_2)_2O]}\right)_t = -0.0132_5\ \text{min}^{-1} \bullet t + \ln\left(P_{[(CH_2)_2O]}\right)_0$$

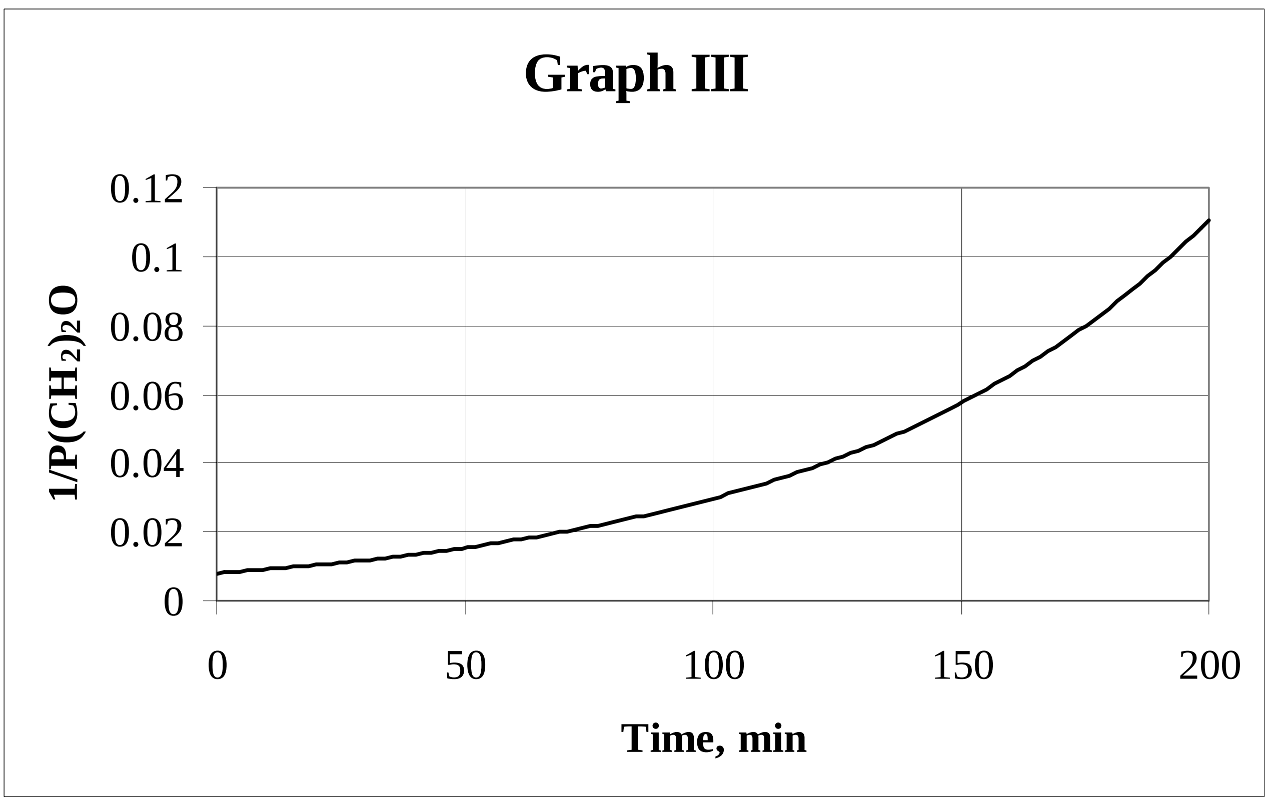
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0132_5\ \text{min}^{-1}} = 52.3\ \text{min}$$

Which expression we use depends upon what we want to know about the reaction: rate, final or initial concentrations, half life, or time. We choose the expression that has the value we wish to solve for based on the given values.


Graph 0
140
120
100
80
60
40
20
0
P, mmHg
0
20
40
60
80
100
120
140
160
180
200
Time, min
CH4
(CH2)2O


Graph I
140
120
100
80
60
40
20
0
Time, min
0
50
100
150
200
P(CH2)2O, mmHg


Graph II
y = -0.0131x + 4.8278
R2 = 1
ln(P[CH2)2O]
5
4.5
4
3.5
3
2.5
2
0
50
100
150
200
Time, min


Graph III
1/P(CH2)2O
0.12
0.1
0.08
0.06
0.04
0.02
0
0
50
100
150
200
Time, min